

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
12 September 2002 (12.09.2002)

PCT

(10) International Publication Number
WO 02/070631 A2

(51) International Patent Classification⁷: **C10G 65/16**

(21) International Application Number: **PCT/EP02/02452**

(22) International Filing Date: **5 March 2002 (05.03.2002)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
01400561.5 **5 March 2001 (05.03.2001)** **EP**

(71) Applicant (for all designated States except US): **SHELL
INTERNATIONALE RESEARCH MAATSCHAPPIJ
B.V. [NL/NL];** Carel van Bylandtlaan 30, NL-2596 HR
The Hague (NL).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **GERMAINE,
Gilbert, Robert, Bernard [FR/FR];** Route Departemen-
tale n° 3, F-76650 Petit Couronne (FR).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

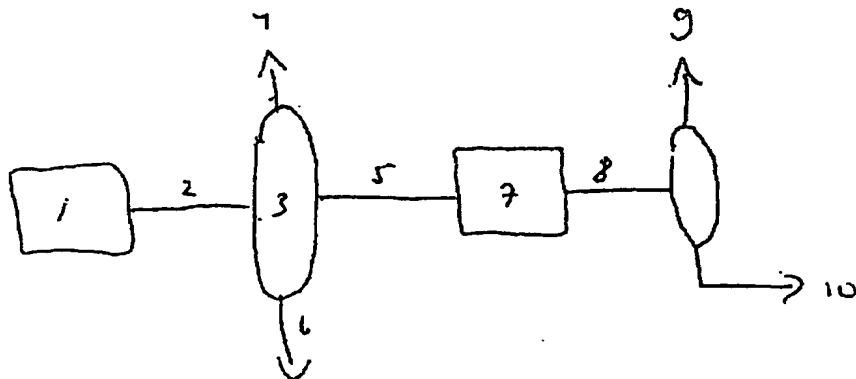
(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **PROCESS TO PREPARE A LUBRICATING BASE OIL**



(57) Abstract: Process to prepare two or more base oil grades, which base oil grades having different kinematic viscosity's at 100°C from a waxy paraffinic Fischer-Tropsch product having a content of non-cyclic iso-paraffins of more than 70 wt% by (a) obtaining from the waxy paraffinic Fischer-Tropsch product a distillate fraction having a viscosity corresponding to one of the desired base oil products, (b) performing a catalytic dewaxing step using the distillate fraction obtained in step (a) as feed, (c) separating the lower boiling compounds from the

dewaxed product obtained in step (b) in order to obtain the desired base oil, and (d) repeating steps (a)-(c) for each base oil.

WO 02/070631 A2

PROCESS TO PREPARE A LUBRICATING BASE OIL

The invention is directed to a process to prepare a base oil from a waxy paraffinic Fischer-Tropsch product having a content of non-cyclic iso-paraffins of more than 80 wt%.

5 Such a process is known from EP-A-776959. This publication describes a process wherein the high boiling fraction of a Fischer-Tropsch synthesis product is first hydroisomerised in the presence of a silica/alumina supported Pd/Pt catalyst. The isomerised product having a
10 content of non-cyclic iso-paraffins of more than 80 wt% is subsequently subjected to a pour point reducing step. The disclosed pour point reducing step in one of the examples is a catalytic dewaxing step performed in the presence of a silica-supported dealuminated ZSM-23
15 catalyst at 310 °C.

A disadvantage of such a process is that only one grade of base oils is prepared. A next disadvantage is that the hydroisomerisation step is performed on a narrow boiling range fraction of a Fischer-Tropsch synthesis
20 product, which hydroisomerisation step is especially directed to prepare a base oil precursor fraction having the desired properties. The hydroisomerisation process step can also yield valuable large volumes of middle distillates next to base oil precursor fractions if the
25 feed would also include more lower boiling compounds. There is thus a desire to prepare base oils from a waxy paraffinic fraction as obtainable from a hydroisomerisation process step, which yields both middle distillates, such as naphtha, kerosine and gas oil, and
30 the waxy paraffinic fraction having a content of non-cyclic paraffins of more than 80 wt%. There is also a

desire to have a flexible process wherein two or more base oils having different viscosity properties are obtained of excellent quality.

5 The object of the present invention is to provide a process wherein two or more high quality base oils are prepared having different viscosities from a waxy Fischer-Tropsch product.

10 The following process achieves this object. Process to prepare two or more base oil grades, which base oil grades having different kinematic viscosities at 100 °C from a waxy paraffinic Fischer-Tropsch product having a content of non-cyclic iso-paraffins of more than 70 wt% by

- 15 (a) obtaining from the waxy paraffinic Fischer-Tropsch product a distillate fraction having a viscosity corresponding to one of the desired base oil products,
(b) performing a pour point reducing step using the distillate fraction obtained in step (a) as feed,
(c) optionally separating the lower boiling compounds
20 from the dewaxed product obtained in step (b) in order to obtain the desired base oil, and
(d) repeating steps (a)-(c) for each base oil.

Applicants found that by performing the process in the afore mentioned manner a haze free base oil grade
25 having also other excellent quality properties can be prepared. A further advantage is that in step (c) no higher boiling compounds need to be removed. Thus an energy consuming distillation step can be omitted. The advantages are even higher when two or more base oils are
30 prepared having a difference in kinematic viscosity at 100 °C of less than 2 cSt.

The waxy paraffinic Fischer-Tropsch product having the high content of non-cyclic iso-paraffins of more than 70 wt%, preferably more than 80 wt%, can be obtained by
35 well-known processes, for example the so-called

commercial Sasol process, the Shell Middle Distillate Process or by the non-commercial Exxon process. These and other processes are for example described in more detail in EP-A-776959, EP-A-668342, US-A-4943672, US-A-5059299, WO-A-9934917 and WO-A-9920720. The process will generally comprise a Fischer-Tropsch synthesis and a hydroisomerisation step as described in these publications. The hydroisomerisation step is needed to obtain the required content of non-cyclic iso-paraffins in the feed.

In step (a) a distillate fraction having a viscosity corresponding to one of the desired base oil products is obtained from the waxy paraffinic Fischer-Tropsch product. Step (a) is suitably performed by means of distillation of a hydroisomerisation product. The distillation step may include a first distillation at about atmospheric conditions, preferably at a pressure of between 1.2-2 bara, wherein lower boiling fractions, for example naphtha, kerosine and gas oil are separated from a higher boiling fraction. The higher boiling fraction, of which suitably at least 95 wt% boils above 350 °C, preferably above 370 °C, is subsequently further separated in a vacuum distillation step wherein a vacuum gas oil fraction, the distillate base oil precursor fraction and a higher boiling fraction are obtained. The vacuum distillation is suitably performed at a pressure of between 0.001 and 0.05 bara. When the waxy paraffinic Fischer-Tropsch product is a high boiling mixture, having an initial boiling point of between 330 and 400 °C, an atmospheric distillation step may suitably be omitted.

The distillate fraction, or the distillate base oil precursor fraction as obtained in step (a), has a viscosity corresponding to the desired viscosity of the base oil product.

For targeted base oils having a kinematic viscosity at 100 °C of between 4.5 and 6 cSt the kinematic

viscosity at 100 °C of the distillate fraction is preferably between 0.05 and 0.3 cSt lower than the target viscosity of the base oil. More preferably the kinematic viscosity at 100 °C of the distillate fraction as
5 obtained in step (a) is between $0.8 \cdot P$ and $1.2 \cdot P$, wherein

$$P = \nu K@100p - \Delta PP/200.$$

In the above formula $\nu K@100p$ is the kinematic viscosity at 100 °C of the base oil product as to be obtained in step (c) expressed in centistokes and ΔPP is the absolute
10 difference in pour point of said fraction obtained in step (a) and said product obtained in step (c) in degrees Celsius. Even more preferably said viscosity is between $0.9 \cdot P$ and $1.1 \cdot P$ and most preferably about 1.

The kinematic viscosity at 100 °C of the distillate
15 fraction is preferably between 3 and 10 cSt. Suitable distillate fractions obtained in step (a) have a T10 wt% boiling point of between 200 and 450 °C and a T90 wt% boiling point of between 300 and 650 more preferably between 300 and 550 °C.

In a preferred embodiment a first base oil grade having a kinematic viscosity at 100 °C of between 3.5 and 4.5 cSt and a second base oil grade having a kinematic viscosity at 100 °C of between 4.5 and 5.5 cSt are advantageously prepared in high yields by performing
20 step (a) in a first mode (v1) to obtain a base oil precursor fraction having a kinematic viscosity at 100 °C corresponding to the first base oil grade and in a second mode (v2) to obtain a base oil precursor fraction having a kinematic viscosity at 100 °C corresponding to the
25 second base oil grade. By performing the pour point reducing step (b) separately on the first and second base oil precursor fractions high quality base oils can be
30 obtained.

In step (b) the distillate base oil precursor fraction obtained in step (a) is subjected to a pour point reducing treatment. With a pour point reducing treatment is understood every process wherein the pour point of the base oil is reduced by more than 10 °C, preferably more than 20 °C, more preferably more than 25 °C.

The pour point reducing treatment can be performed by means of a so-called solvent dewaxing process or by means of a catalytic dewaxing process. Solvent dewaxing is well known to those skilled in the art and involves admixture of one or more solvents and/or wax precipitating agents with the base oil precursor fraction and cooling the mixture to a temperature in the range of from -10 °C to -40 °C, preferably in the range of from -20 °C to -35 °C, to separate the wax from the oil. The oil containing the wax is usually filtered through a filter cloth which can be made of textile fibres, such as cotton; porous metal cloth; or cloth made of synthetic materials. Examples of solvents which may be employed in the solvent dewaxing process are C₃-C₆ ketones (e.g. methyl ethyl ketone, methyl isobutyl ketone and mixtures thereof), C₆-C₁₀ aromatic hydrocarbons (e.g. toluene), mixtures of ketones and aromatics (e.g. methyl ethyl ketone and toluene), autorefrigerative solvents such as liquefied, normally gaseous C₂-C₄ hydrocarbons such as propane, propylene, butane, butylene and mixtures thereof. Mixtures of methyl ethyl ketone and toluene or methyl ethyl ketone and methyl isobutyl ketone are generally preferred. Examples of these and other suitable solvent dewaxing processes are described in Lubricant Base Oil and Wax Processing, Avilino Sequeira, Jr, Marcel Dekker Inc., New York, 1994, Chapter 7.

Preferably step (b) is performed by means of a catalytic dewaxing process. With such a process it has

been found that base oils having a pour point of below -40 °C can be prepared when starting from a base oil precursor fraction as obtained in step (a) of the present process.

5 The catalytic dewaxing process can be performed by any process wherein in the presence of a catalyst and hydrogen the pour point of the base oil precursor fraction is reduced as specified above. Suitable dewaxing catalysts are heterogeneous catalysts comprising a
10 molecular sieve and optionally in combination with a metal having a hydrogenation function, such as the Group VIII metals. Molecular sieves, and more suitably intermediate pore size zeolites, have shown a good catalytic ability to reduce the pour point of the
15 distillate base oil precursor fraction under catalytic dewaxing conditions. Preferably the intermediate pore size zeolites have a pore diameter of between 0.35 and 0.8 nm. Suitable intermediate pore size zeolites are ZSM-5, ZSM-12, ZSM-22, ZSM-23, SSZ-32, ZSM-35 and ZSM-48.
20 Another preferred group of molecular sieves are the silica-aluminaphosphate (SAPO) materials of which SAPO-11 is most preferred as for example described in US-A-4859311. ZSM-5 may optionally be used in its HZSM-5 form in the absence of any Group VIII metal. The other
25 molecular sieves are preferably used in combination with an added Group VIII metal. Suitable Group VIII metals are nickel, cobalt, platinum and palladium. Examples of possible combinations are Ni/ZSM-5, Pt/ZSM-23, Pd/ZSM-23, Pt/ZSM-48 and Pt/SAPO-11. Further details and examples of
30 suitable molecular sieves and dewaxing conditions are for example described in WO-A-9718278, US-A-5053373, US-A-5252527 and US-A-4574043.

 The dewaxing catalyst suitably also comprises a binder. The binder can be a synthetic or naturally
35 occurring (inorganic) substance, for example clay, silica

and/or metal oxides. Natural occurring clays are for example of the montmorillonite and kaolin families. The binder is preferably a porous binder material, for example a refractory oxide of which examples are:

5 alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions for example silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. More preferably a

10 low acidity refractory oxide binder material which is essentially free of alumina is used. Examples of these binder materials are silica, zirconia, titanium dioxide, germanium dioxide, boria and mixtures of two or more of these of which examples are listed above. The most

15 preferred binder is silica.

A preferred class of dewaxing catalysts comprise intermediate zeolite crystallites as described above and a low acidity refractory oxide binder material which is essentially free of alumina as described above, wherein

20 the surface of the aluminosilicate zeolite crystallites has been modified by subjecting the aluminosilicate zeolite crystallites to a surface dealumination treatment. A preferred dealumination treatment is by contacting an extrudate of the binder and the zeolite

25 with an aqueous solution of a fluorosilicate salt as described in for example US-A-5157191 or WO-A-0029511. Examples of suitable dewaxing catalysts as described above are silica bound and dealuminated Pt/ZSM-5, silica bound and dealuminated Pt/ZSM-23, silica bound and

30 dealuminated Pt/ZSM-12, silica bound and dealuminated Pt/ZSM-22 as for example described in WO-A-0029511 and EP-B-832171.

Catalytic dewaxing conditions are known in the art and typically involve operating temperatures in the range

35 of from 200 to 500 °C, suitably from 250 to 400 °C,

hydrogen pressures in the range of from 10 to 200 bar, preferably from 40 to 70 bar, weight hourly space velocities (WHSV) in the range of from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l/hr), suitably from 0.2 to 5 kg/l/hr, more suitably from 0.5 to 3 kg/l/hr and hydrogen to oil ratios in the range of from 100 to 2,000 litres of hydrogen per litre of oil. By varying the temperature between 275 and suitably between 315 and 375 °C at between 40-70 bars, in the catalytic dewaxing step it is possible to prepare base oils having different pour point specifications varying from suitably lower than -60 to -10 °C.

After performing a catalytic dewaxing step (b) lower boiling compounds formed during catalytic dewaxing are removed in step (c), preferably by means of distillation, optionally in combination with an initial flashing step.

In step (d) steps (a)-(c) are repeated for every desired base oil.

In a preferred embodiment a first base oil (grade-4) is prepared having a kinematic viscosity at 100 °C of between 3.5 and 4.5 cSt (according to ASTM D 445), a volatility of below 20 wt% and preferably below 14 wt% (according to CEC L40 T87) and a pour point of between -15 and -60 °C (according to ASTM D 97), more preferably between -25 and -60 °C, by catalytic dewaxing in step (b) a distillate fraction obtained in step (a) having a kinematic viscosity at 100 °C of between 3.2 and 4.4 cSt and a second base oil (grade 5) is prepared having a kinematic viscosity at 100 °C of between 4.5 and 5.5, a volatility of below 14 wt% and preferably below 10 wt% and a pour point of between -15 and -60 °C), more preferably between -25 and -60 °C, by catalytic dewaxing in step (b) a distillate fraction obtained in step (a) having a kinematic viscosity at 100 °C of between 4.2 and 5.4 cSt.

Figure 1 shows a preferred embodiment of the process according the present invention. In a process (1) a waxy paraffinic Fischer-Tropsch product (2) is prepared having a content of non-cyclic iso-paraffins of more than
5 70 wt%. From this product (2) a distillate fraction (5) is obtained in distillation column (3) by separating of a light (4) and heavy fraction (6). This fraction (5) has a viscosity which corresponds with the desired base oil grade (10). In reactor (7) a catalytic dewaxing step is
10 performed on the fraction (5) thereby obtaining a dewaxed oil (8). By separating off light fraction (9) in distillation column (11) the desired base oil grade (10) is obtained. By variation of the separation in distillation column (3) the properties of base oil
15 grade (10) can be varied according to the process of the present invention.

The above-described Base oil grade-4 can suitably find use as base oil for an Automatic Transmission Fluids (ATF). If the desired kinematic viscosity at 100 °C
20 (vK@100) of the ATF is between 3 and 3.5 cSt, the Base Oil grade-4 is suitably blended with a grade having a vK@100 of about 2 cSt. The base oil (grade-2) having a kinematic viscosity at 100 °C of about 2 to 3 cSt can suitably be obtained by catalytic dewaxing of a suitable
25 gas oil fraction as obtained in the atmospheric distillation in step (a) as described above. The Automatic Transmission Fluid will comprise the base oil (blend) as described above, preferably having a vK@100 of between 3 and 6 cSt, and one or more additives. Examples
30 of additives are antiwear, antioxidant, and viscosity modifier additives.

The invention is furthermore directed to a novel class of base oils having a saturates content of above
35 95 wt%, preferably above 97 wt%, a kinematic viscosity at 100 °C of between 8 and 12 cSt, preferably above 8.5 cSt

and a pour point of below -30°C and a viscosity index of above 120 preferably above 130. The combination of such low pour point high viscosity index fluids containing almost only cyclo, normal and iso-paraffins is considered novel. Such base oils may be advantageously used as white oils in medicinal or food applications. To obtain a base oil having the desired colour specification it may be required to hydrofinish the base oil, for example using a noble metal hydrofinishing catalyst C-624 of Criterion Catalyst Company, or by contacting the base oil with active carbon. Base oils having a colour according to ASTM D 1500 of less than 0.5 and according to ASTM D 156 Saybolt of greater than +10 and even equal to +30 can thus be obtained.

The base oils obtained by the present process having intermediate vK@100 values of between 2 and 9 cSt, of which preferred grade-4 and grade-5 have been described above, are preferably used as base oil in formulations such as gasoline engine oils, diesel engine oils, electrical oils or transformer oils and refrigerator oils. The use in electrical and refrigerator oils is advantageous because of the naturally low pour point when such a base oil, especially the grades having a pour point of below -40°C , is used to blend such a formulation. This is advantageous because the highly iso-paraffinic base oil has a naturally high resistance to oxidation compared to low pour point naphthenic type base oils. Especially the base oils having the very low pour points, suitably lower than -40°C , have been found to be very suitable for use in lubricant formulations such as gasoline and diesel engine oils of the 0W-x specification according to the SAE J-300 viscosity classification, wherein x is 20, 30, 40, 50 or 60. It has been found that these high tier lubricant formulations can be prepared with the base oils obtainable by the process of the

current invention. Other gasoline and diesel engine oil applications are the 5W-x and the 10W-x formulations, wherein the x is as above. The gasoline oil formulation will suitably comprise the above-described base oil and one or more of additives. Examples of additive types which may form part of the composition are dispersants, detergents, viscosity modifying polymers, extreme pressure/antiwear additives, antioxidants, pour point depressants, emulsifiers, demulsifiers, corrosion inhibitors, rust inhibitors, antistaining additives, friction modifiers. Specific examples of such additives are described in for example Kirk-Othmer Encyclopedia of Chemical Technology, third edition, volume 14, pages 477-526.

The invention will be illustrated by the following non-limiting examples.

Example 1

1000 g per hour of a distillate fraction of an isomerised Fischer-Tropsch product having the properties as Feed N°1 in Table 1 was fed to a catalytic dewaxing reactor. The effluent of the catalytic dewaxing reactor was topped at 390 °C to remove only the light boiling fraction. The thus obtained base oil was recovered in a 69 wt% yield based on Feed N°1. The dewaxing conditions are as in Table 2. The catalyst used in the dewaxing step was a Pt/silica bound ZSM-5 catalyst as described in Example 9 of WO-A-0029511. The properties of the thus obtained base oils are in Table 3.

Example 2

Example 1 was repeated except at different dewaxing conditions (see Table 2). The properties of the base oil are in Table 3.

Table 1

| Feed No. | 1 | 2 |
|------------------------------------|-------|-------|
| Density at 70 °C | 784.8 | 784.5 |
| T10 wt% boiling point (°C) | 407 | 346 |
| T90 wt% boiling point (°C) | 520 | 610 |
| Kinematic viscosity at 10 °C (cSt) | 5.151 | 6.244 |
| Pour point (°C) | +46 | +30 |

Table 2

| Dewaxing conditions | Example 1 | Example 2 |
|---------------------------------------|-----------|-----------|
| Reactor temperature (°C) | 325 | 342 |
| Hydrogen pressure (bar) | 37 | 36 |
| Weight hourly space velocity (kg/l/h) | 1.0 | 1.0 |
| Hydrogen flow rate (Nl/h) | 700 | 700 |

Table 3

| | Example 1 | Example 2 |
|---------------------------------------|------------|------------|
| Feed | Feed No. 1 | Feed No. 1 |
| Base oil properties | | |
| Density at 20 °C (kg/m ³) | 819.7 | 819.0 |
| Kinematic viscosity at 100 °C (cSt) | 5.51 | 5.41 |
| Pour Point (°C) | -20 | -48 |
| Noack (wt%) | 6.3 | 7.4 |

Example 3

Example 1 was repeated at the conditions described in Table 4 using Feed No. 2 (see Table 1). The properties of the resulting base oil are presented in Table 5.

Example 4

Example 1 was repeated at the conditions described in Table 4 using Feed No. 2 (see Table 1). The properties of the resulting base oil are presented in Table 5.

Table 4

| Dewaxing conditions | Feed 2 Example 3 | Feed 2 Example 4 |
|--|---------------------|---------------------|
| Reactor temperature (°C) | 290 | 296 |
| Hydrogen pressure (bar) | 48 | 47 |
| Weight hourly space velocity (kg/l/h) | 1.0 | 1.0 |
| Hydrogen flow rate (Nl/h) | 750 | 750 |

Table 5

| Base oil properties | Feed 2 Example 1 | Feed 2 Example 2 |
|--|---------------------|---------------------|
| Density at 20 °C (kg/m ³) | 826 | 825.9 |
| Kinematic viscosity at 100 °C (cSt) | 9.78 | 9.75 |
| Viscosity index | 151 | 151 |
| Pour Point (°C) | -9 | -30 |
| Noack (wt%) | 6.1 | 6.0 |

5 The above experiments illustrate that base oils
 having a kinematic viscosity at 100 °C in the range of 3
 to 12 cSt and especially 4 to 12 cSt having excellent
 properties like pour point and viscosity index can be
 obtained using the process according to the invention. It
 10 will be clear that by performing step (a) and (b) in a
 controlled manner according to the present invention all
 viscosity grades in that range can be sequentially
 obtained.

C L A I M S

1. Process to prepare two or more base oil grades, which base oil grades having different kinematic viscosity's at 100 °C from a waxy paraffinic Fischer-Tropsch product having a content of non-cyclic iso-paraffins of more than
5 70 wt% by

(a) obtaining from the waxy paraffinic Fischer-Tropsch product a distillate fraction having a viscosity corresponding to one of the desired base oil products,

(b) performing a catalytic dewaxing step using the
10 distillate fraction obtained in step (a) as feed,
(c) separating the lower boiling compounds from the dewaxed product obtained in step (b) in order to obtain the desired base oil, and

(d) repeating steps (a)-(c) for each base oil.

15 2. Process according to claim 1, wherein the waxy paraffinic Fischer-Tropsch product has a content of non-cyclic iso-paraffins of more than 80 wt%.

3. Process according to any one of claims 1-2, wherein the difference in kinematic viscosity at 100 °C of the
20 different base oil grades is less than 2 cSt.

4. Process according to any one of claims 1-3, wherein the distillate fraction has a T10 wt% boiling point of between 200 and 450 °C and a T90 wt% boiling point of between 300 and 550 °C.

25 5. Process according to claim 4, wherein the distillate fraction has a kinematic viscosity at 100 °C of between 3 and 10 cSt.

6. Process according to any one of claims 1-5, wherein step (b) is performed by means of solvent dewaxing.

30 7. Process according to any one of claims 1-5, wherein step (b) is performed by means of catalytic dewaxing.

8. Process according to claim 7, wherein the catalytic dewaxing is performed in the presence of a catalyst comprising a Group VIII metal, an intermediate pore size zeolite having pore diameter between 0.35 and 0.8 nm, and a low acidity refractory binder which binder is essentially free of alumina.

9. Process according to any one of claims 1-8, wherein a base oil having a kinematic viscosity at 100 °C of between 4.5 and 6 cSt is prepared and wherein the kinematic viscosity at 100 °C of the distillate fraction as obtained in step (a) is between $0.8 \cdot P$ and $1.2 \cdot P$, wherein $P = vK@100p - \Delta PP/200$,

in which equation $vK@100p$ is the kinematic viscosity at 100 °C of the base oil product as obtained in step (c) and ΔPP is the absolute difference in pour point of said fraction obtained in step (a) and said product obtained in step (c) in degrees Celsius.

10. Process according to claim 9, wherein the kinematic viscosity at 100 °C of the distillate fraction as obtained in step (a) is between $0.9 \cdot P$ and $1.1 \cdot P$.

11. Process according to claim 10, wherein the kinematic viscosity at 100 °C of the distillate fraction as obtained in step (a) is about equal to p .

12. Process according to any one of claims 1-11, wherein a first base oil is prepared having a kinematic viscosity at 100 °C of between 3.5 and 4.5 cSt, a volatility of below 11 wt% and a pour point of between -15 and -60 °C by catalytic dewaxing in step (b) a distillate fraction obtained in step (a) having a kinematic viscosity at 100 °C of between 3.2 and 4.4 cSt and a second base oil is prepared having a kinematic viscosity at 100 °C of between 4.5 and 5.5, a volatility of below 14 wt% and a pour point of between -15 and -60 °C by catalytic dewaxing in step (b) a distillate fraction obtained in

step (a) having a kinematic viscosity at 100 °C of between 4.2 and 5.4 cSt.

13. Passenger car motor oil comprising one of the base oils as obtained by the process according to claim 10.

5 14. Base oil having a saturates content of above 97 wt%, a kinematic viscosity at 100 °C of between 8 and 12 cSt, a pour point of below -30 °C and a viscosity index of above 120.

10 15. Base oil according to claim 14, wherein the kinematic viscosity at 100 °C is higher than 8.5 cSt and the viscosity index is above 130.

15 16. Base oil according to any one of claims 14-15, wherein the colour of the base oil is a colour according to ASTM D 1500 of less than 0.5 and according to ASTM D 156 Saybolt of between +10 and +30.

17. Base oil according to any one of claims 14-16 as obtained by the process according to claim 7.

20 18. Use of the base oil according to any one of claims 14-17 as a white oil in medicinal or food applications.

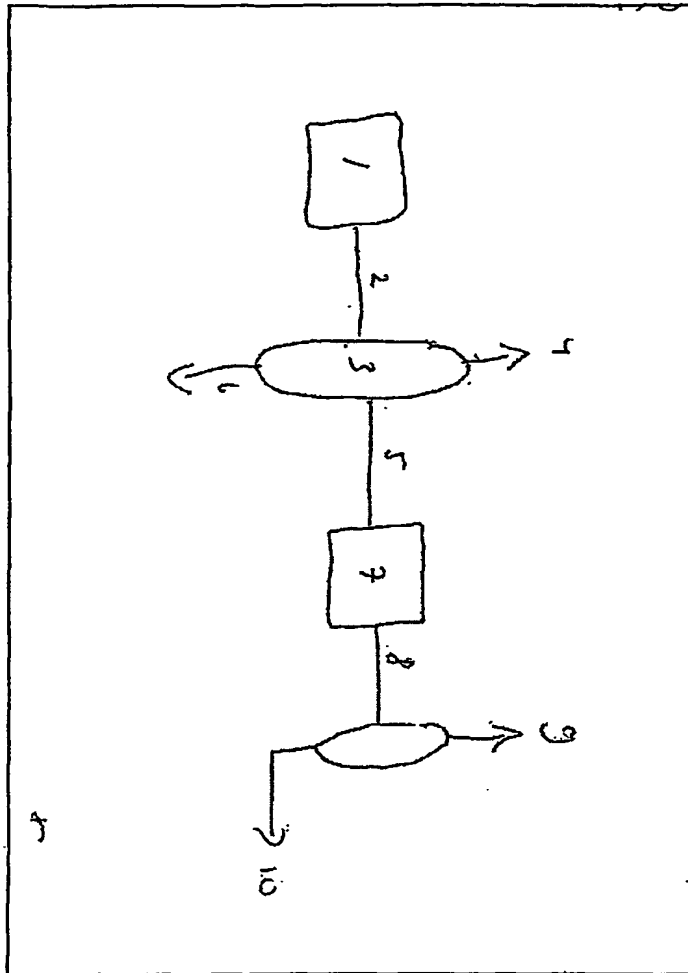


Fig. 1

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
12 September 2002 (12.09.2002)

PCT

(10) International Publication Number
WO 02/070631 A3

(51) International Patent Classification⁷: **C10G 65/16**

(21) International Application Number: PCT/EP02/02452

(22) International Filing Date: 5 March 2002 (05.03.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01400561.5 5 March 2001 (05.03.2001) EP

(71) Applicant (for all designated States except US): **SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

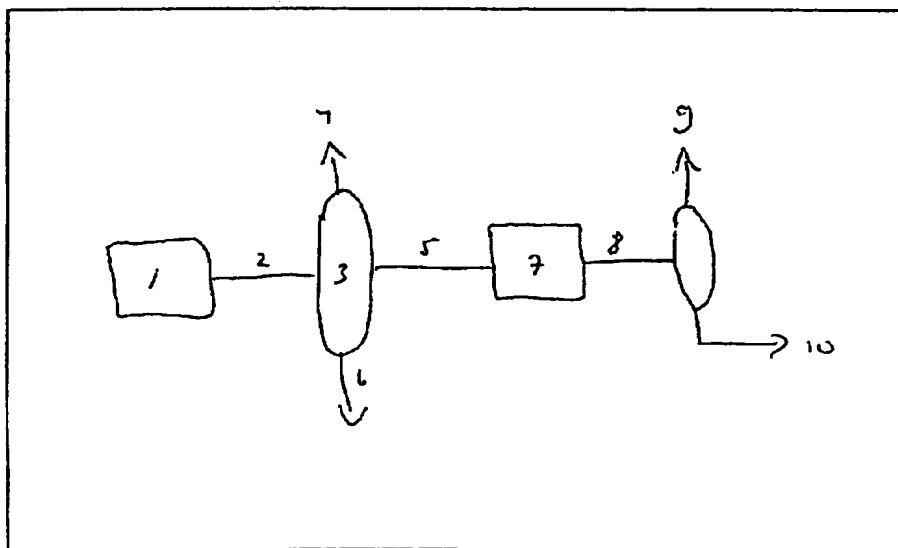
Published:

— with international search report

(88) Date of publication of the international search report:
24 July 2003

[Continued on next page]

(54) Title: PROCESS TO PREPARE A LUBRICATING BASE OIL



(57) Abstract: Process to prepare two or more base oil grades, which base oil grades having different kinematic viscosity's at 100°C from a waxy paraffinic Fischer-Tropsch product having a content of non-cyclic iso-paraffins of more than 70 wt% by (a) obtaining from the waxy paraffinic Fischer-Tropsch product a distillate fraction having a viscosity corresponding to one of the desired base oil products, (b) performing a catalytic dewaxing step using the distillate fraction obtained in step (a) as feed, (c) separating the lower boiling compounds from the dewaxed product obtained in step (b) in order to obtain the desired base oil, and (d) repeating steps (a)-(c) for each base oil.

WO 02/070631 A3



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/02452

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10G65/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| Y | EP 0 776 959 A (SHELL INT RESEARCH) 4 June 1997 (1997-06-04) cited in the application the whole document | 1-8, 12, 13 |
| Y | EP 0 237 655 A (SHELL INT RESEARCH) 23 September 1987 (1987-09-23) the whole document | 1-8, 12, 13 |
| A | US 3 876 522 A (CAMPBELL IAN D ET AL) 8 April 1975 (1975-04-08) the whole document | 1-13 |
| A | WO 98 02503 A (CHEVRON USA INC) 22 January 1998 (1998-01-22) the whole document | 1-13 |
| | -/- | |



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * & * document member of the same patent family

Date of the actual completion of the international search

4 April 2003

Date of mailing of the international search report

11 04 2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

De Herdt, O.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/02452

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| A | WO 00 14184 A (EXXON RESEARCH ENGINEERING CO) 16 March 2000 (2000-03-16) the whole document | 1-13 |
| A | US 5 372 703 A (KAMIYA KOUZOU (JP) NULL ET AL) 13 December 1994 (1994-12-13) claims 1,6 column 6, line 16 - line 18 table 7 | 14,17 |
| A | US 6 059 955 A (CODY IAN A (US) NULL ET AL) 9 May 2000 (2000-05-09) claim 1 column 1, line 62 - line 67 | 14-16 |

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 02/02452

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-13

A process to prepare two or more base oils with different kinematic viscosities at 100°C from a waxy Fischer-Tropsch product having a content of non-cyclic isoparaffins of greater than 70 %, by a catalytic dewaxing operation followed by separation of the lower boiling components from the dewaxed product.

2. claims: 14-18

A base oil having a saturates content of above 97 %, a kinematic viscosity at 100 °C of between 8 and 12 cSt, a pour point of below -30 °C and a viscosity index of at least 120.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/02452

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|---|---------------------|--|--|
| EP 0776959 | A | 04-06-1997 | EP 0776959 A2 AU 705415 B2 AU 7198896 A CA 2191290 A1 CN 1167811 A , B JP 9221685 A SG 74001 A1 TW 416981 B ZA 9609906 A | 04-06-1997 20-05-1999 05-06-1997 29-05-1997 17-12-1997 26-08-1997 18-07-2000 01-01-2001 28-05-1997 |
| EP 0237655 | A | 23-09-1987 | AU 592137 B2 AU 6663986 A BR 8606234 A CA 1282363 A1 CN 86108258 A , B DE 3685578 D1 DE 3685578 T2 EP 0237655 A1 ES 2031820 T3 IN 168775 A1 JP 62190286 A KR 9408389 B1 SG 44393 G | 04-01-1990 25-06-1987 29-09-1987 02-04-1991 28-10-1987 09-07-1992 21-01-1993 23-09-1987 01-01-1993 01-06-1991 20-08-1987 14-09-1994 25-06-1993 |
| US 3876522 | A | 08-04-1975 | NONE | |
| WO 9802503 | A | 22-01-1998 | AU 724363 B2 AU 3664997 A BR 9710326 A CZ 9900096 A3 EA 1619 B1 EP 0912660 A1 HU 0004280 A2 JP 2000515185 T KR 2000023803 A PL 331037 A1 TR 9900097 T2 TW 399092 B WO 9802503 A1 | 21-09-2000 09-02-1998 17-08-1999 14-04-1999 25-06-2001 06-05-1999 28-04-2001 14-11-2000 25-04-2000 21-06-1999 22-03-1999 21-07-2000 22-01-1998 |
| WO 0014184 | A | 16-03-2000 | US 6179994 B1 AU 752602 B2 AU 5693899 A BR 9913412 A CA 2340627 A1 EP 1144552 A2 JP 2002527530 T NO 20011000 A WO 0014184 A2 US 6375830 B1 | 30-01-2001 26-09-2002 27-03-2000 22-05-2001 16-03-2000 17-10-2001 27-08-2002 04-05-2001 16-03-2000 23-04-2002 |
| US 5372703 | A | 13-12-1994 | JP 2938487 B2 JP 3223393 A JP 2724508 B2 JP 4036391 A JP 2724510 B2 JP 4068082 A JP 2724512 B2 | 23-08-1999 02-10-1991 09-03-1998 06-02-1992 09-03-1998 03-03-1992 09-03-1998 |

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|---|---------------------|----------------------------|---------------------|
| US 5372703 | A | | JP 4120193 A | 21-04-1992 |
| | | | DE 69011829 D1 | 29-09-1994 |
| | | | DE 69011829 T2 | 13-04-1995 |
| | | | EP 0435670 A1 | 03-07-1991 |
| US 6059955 | A | 09-05-2000 | AU 742299 B2 | 20-12-2001 |
| | | | AU 2765199 A | 30-08-1999 |
| | | | CA 2319531 A1 | 19-08-1999 |
| | | | EP 1062305 A1 | 27-12-2000 |
| | | | JP 2002503752 T | 05-02-2002 |
| | | | WO 9941332 A1 | 19-08-1999 |